

The Rates of the Reactions in Solutions
Containing Ferrous Sulphate, Potas-
sium Iodide, and Chromic Acid

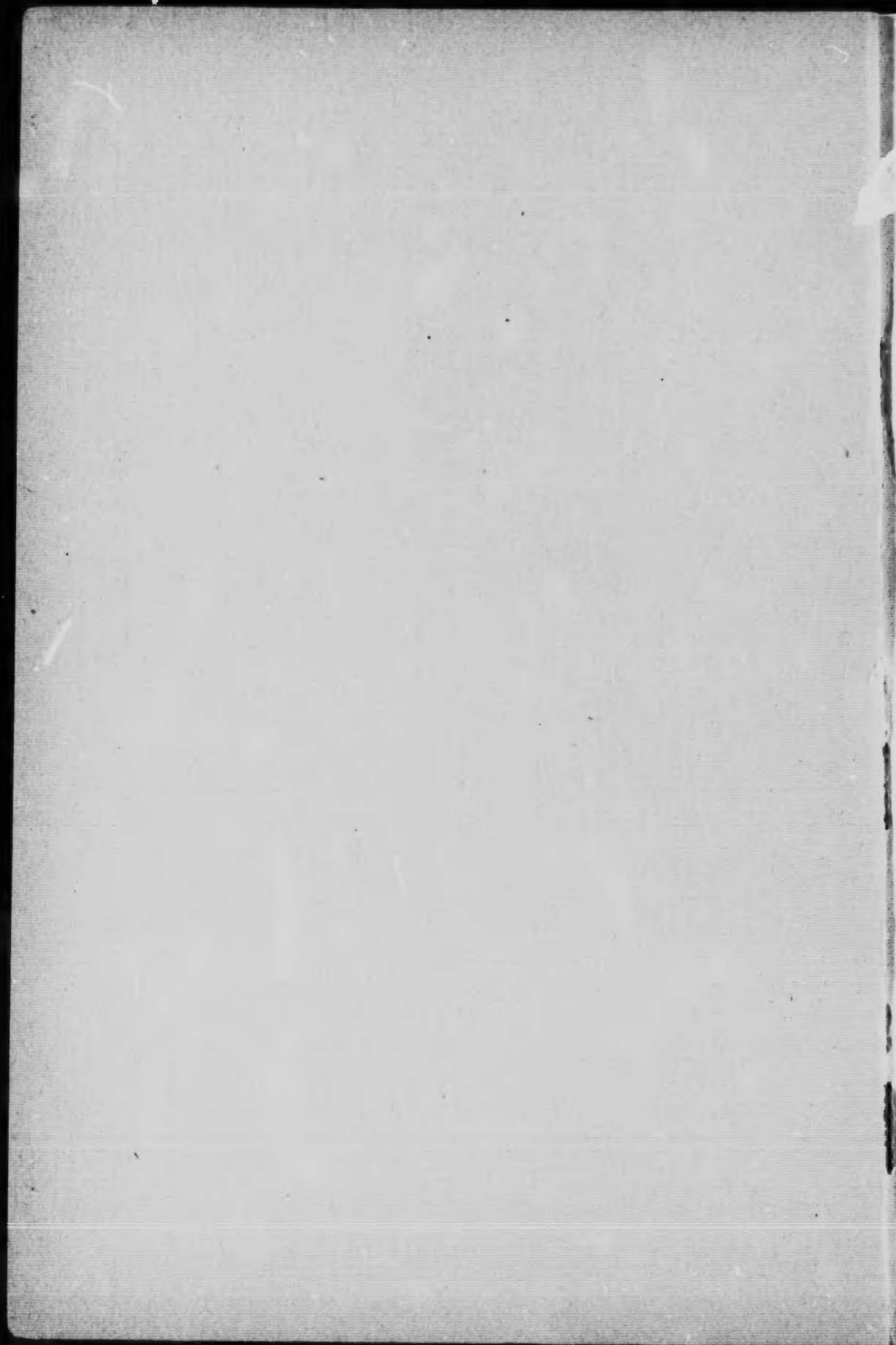
THESIS

PRESENTED TO THE SENATE OF THE UNIVERSITY OF TORONTO
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

CLARA C. BENSON

Reprinted from The Journal of Physical Chemistry May 1903



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To the Senate of the University of Toronto :

I beg to report that Miss Clara C. Benson, a candidate for the degree of Doctor of Philosophy, has passed a satisfactory examination in Physical Chemistry, her major subject ; and I recommend that her thesis, " The Rates of the Reactions in Solutions Containing Ferrous Sulphate, Potassium Iodide, and Chromic Acid " be accepted for the degree.

W. LASH MILLER,

Toronto, May, 1903.

Associate-Professor of Physical Chemistry.

I hereby certify that the thesis above mentioned has been accepted by the Senate of the University of Toronto for the degree of Doctor of Philosophy, in accordance with the terms of the statute in that behalf.

The University of Toronto,

JAMES BREBNER,

June, 5, 1903.

Registrar.

TABLE OF CONTENTS

INTRODUCTION	
Résumé	5
Method of carrying out the experiments.....	6
Solutions employed	8
RESULTS OF THE MEASUREMENTS	
Explanation of the tables.....	8
The rate of liberation of iodine :	
Influence of the acid	9
Influence of the potassium bichromate	9
Influence of the potassium iodide	10
Influence of the ferrous salt.....	11
Influence of the products of oxidation.....	11
Influence of certain other compounds of iron	12
The rate of oxidation of the ferrous salt :	
Method of analysis.....	13
Influence of the concentrations of the reagents	14
Summary of the results of the measurements.....	14
COMPARISON OF THE RESULTS OF THE MEASUREMENTS WITH THE REQUIREMENTS OF CERTAIN THEORIES	
The catalytic theory.....	15
The active oxygen theory....	16
The peroxide theory :	
Manchot's views	16
Development of the theory	18
Three special cases.....	20
Discussion.....	22
The ferroiodion theory :	
Advantages.....	23
Possible modifications.....	25
THE EXPERIMENTAL MATERIAL	
Tables I-XXIII....	28 38

THE RATES OF THE REACTIONS IN SOLUTIONS CONTAINING FERROUS SULPHATE, POTAS- SIUM IODIDE, AND CHROMIC ACID

BY CLARA C. BENSON

In this paper, which may be regarded as a sequel to my experiments on the rate of oxidation of ferrous salts by chromic acid,¹ and to those of Mr. R. E. DeLury² on the oxidation of potassium iodide by the same substance, I have determined the effect of the concentrations of the reagents on the rate of oxidation of ferrous sulphate and of potassium iodide in solutions containing both.

After describing the method of working, and arranging the results of the measurements, I have made use of them to discuss the various theories put forward (in advance of rate measurements) to account for the great acceleration often exerted by iron salts on reactions involving oxidation.

Of these the favorite is the "Peroxide Theory", according to which the primary product of the oxidation of iron is a peroxide, which subsequently breaks down into ordinary ferric salts, transferring part of its oxygen to other chemicals ("acceptors") in the process. I have not been able to reconcile the results of my measurements with the consequences of this theory.

Finally, without expressing an opinion on the custom of "explaining" the kinetics of chemical systems by inventing reactions where the formulas are related to the rates by certain rules, I have endeavored to comply with the fashion of the day by setting up a theory of my own — the "Ferroiodion Theory" — which can be brought into accord with the main results of the rate measurements.

The experiments of the present paper have all been carried out at zero; a few at higher temperatures, which show that

¹ Jour. Phys. Chem. 7, 1 (1903).

² Ibid. 7, 239 (1903).

the rate of liberation of iodine is decreased by raising the temperature, will be published separately.

Method of working

The method of carrying out the experiments was much the same as that employed in my measurements of the rate of oxidation of ferrous sulphate. When the standardized solutions had been cooled to 0° in wash-bottles clamped in the thermostat, the amounts necessary for an experiment (100 to 200 cc acid, 100 to 300 cc bichromate, 50 cc oxidation product, 5 to 30 cc potassium iodide), were blown into measuring flasks or pipetted out, and mixed with the proper quantity of water in a beaker suspended in the bath.¹ The whole was well stirred, the ferrous sulphate (measured in a 1 cc pipette divided into 1/100 cc, and diluted with 100 cc water in a Nessler tube) was poured in, and a stop-watch was set in motion by pressing on a pedal.

At the expiration of the desired interval, 10 cc of a half-saturated solution of ammonium bicarbonate was poured in from a test-tube, 5 cc of a filtered 1 percent starch solution was added, and the iodine was determined by $n/100$ sodium arsenite dropping slowly from a burette (1 cc per minute); a Witt stirrer kept the contents of the beaker well mixed.

By adding alternate drops of $n/100$ iodine and arsenite solutions, the end-point could be determined within 0.05 cc. Duplicates however often differed more,² although the probable error in individual experiments does not exceed 5 percent. This includes the uncertainty in the end-point, and the errors in the four burette readings and in measuring out the requisite volumes of water and of five reagents; the extreme variation in the temperature of the reacting mixture never reached 0.5° C.

Owing to the small amount of iodine liberated, an uncertainty of two or three drops of arsenite represents a greater per-

¹ The potassium iodide was diluted with 100 cc water, and added last, just before the ferrous sulphate.

² For instance, *Cr*, 20 cc; *Ac*, 10 cc; *KI*, 20 cc; *Ox*, 5; *F*, 1.0 cc; *θ*, 4; *As* found: — 4.27, 4.22, 4.26, 4.35, 4.25, 4.20, 4.25, 4.35, 4.20, 4.29, in a number of experiments carried out at intervals of weeks.

centage error than is at all desirable; any large increase in the concentrations of the reagents, however, was impossible, owing to the rapidity of the oxidation; while the advantages consequent on working with excess of all the reagents save one could not be dispensed with.

When the volume much exceeded 700 cc the end-point was more difficult of determination, and the readings were subject to a correction for the iodine necessary to give a color. A similar correction of 0.10 cc *As* was necessary when the amount of the potassium iodide used was less than 20 cc (Expts. 14, 15, 16, 17.) The scope of the investigation was further limited by the fact that some of the iodine disappears on adding ammonium bicarbonate, if more than 5 cc of *n*/20 ferrous sulphate remain to be oxidized in the 700 cc of reacting mixture; owing to this circumstance I have not carried out any measurements with ferrous sulphate in excess.

I have assured myself, however, that within the limits to which I have restricted myself, the method of analysis described above yields reliable results.

As iodine is liberated (though very slowly) by the action of chromic acid and of ferric salts on potassium iodide in the absence of ferrous sulphate, it was necessary to undertake a number of blank experiments (in which no ferrous sulphate was added). The duration of these, in minutes, is given after "*Blanks*" at the foot of the tables; a small circle to the right of the number indicates that no free iodine could be detected, an asterisk, liberation of iodine equivalent to one drop (0.05 cc) of *n*/100 arsenite; two asterisks, two drops.

On account of the importance of accurate determinations of the total iodine liberated during the oxidation of a given quantity of iron (y_x), the time of oxidation has been extended in certain cases to one or two hours. In these instances the amount of iodine liberated in the blank experiment is very considerable—it is given with the others at the foot of the Tables, and the amount there stated has been subtracted from the result of the titration to give the figures entered under "*As*" after $\theta = 60$, 120, etc., in the body of the Tables.

Solutions

Solutions of sulphuric acid ($0.059F^1 = 0.1181N$), potassium bichromate ($0.0083F = 0.05N$), potassium iodide ($0.0479F$), and ferrous sulphate² ($0.5F$), were prepared in quantities sufficient to serve for the whole series of measurements; the acid, bichromate and iron were standardized as described in the former paper,³ and the iodide gravimetrically with silver. Before using, the acid, bichromate, and ferrous sulphate were each diluted to ten times the original volume.

The volumetric solution of iodine was compared with the ferrous sulphate by means of permanganate, and was also standardized independently against freshly sublimed iodine.

The "oxidation product" was prepared by making up 200 cc acid, 600 cc bichromate, and 20 cc ferrous sulphate (the undiluted solutions were used) to 2 liters. 50 cc of this contained the product of oxidation of 5 cc $F/20$ ferrous sulphate, and in addition 10 cc $F/120$ bichromate unreduced. This excess of bichromate was taken into consideration in expressing the initial composition of the solutions in the various experiments. A fresh supply of the "oxidation product" was prepared every five or six days.

RESULTS OF THE MEASUREMENTS

Explanation of the Tables

At the head of each table is given the total volume of the reacting mixture and its initial composition, in the following units. *Ac* 10 represents 10 cc of $0.059F$ sulphuric acid; *Cr* 10, 10 cc of $0.0083F$ potassium bichromate, including unreduced bichromate in the oxidation product; *KI* 10, 10 cc of $0.0479F$ potassium iodide; *F* 1.0, 1 cc of $0.05F$ ferrous sulphate; *Ox* 5, the product of oxidation of 5 cc of $0.05F$ ferrous sulphate. Thus the headings give very closely the number of equivalents of the various reagents, one formula weight of bichromate being

¹ One gram formula weight H_2SO_4 in 17.04 liters.

² Free from ferric salt. Jour. Phys. Chem. 7, 5, (1903) footnote.

³ Ibid. 7, 5 (1903).

equivalent to seven of sulphuric acid and to six of ferrous sulphate or of potassium iodide.

Under θ is entered the interval in minutes between the addition of the ferrous sulphate and that of the ammonium bicarbonate; under As the number of cc of $n/100$ sodium arsenite equivalent to the iodine liberated. Under " $Cr\ 20$ " or " $Ac\ 15$ " the number of minutes in which the same amount of iodine was liberated in other experiments where the concentration of the bichromate, or acid, was " 20 " or " 15 " instead of that given at the head of the Table; these numbers were obtained by graphic interpolation from the results of the experiments in question. Under θ/T is entered the quotient of the two times. " $Calc.\ 4th,\ 5.1$," indicates that if the rate were proportional to the fourth power of the concentration of the reagent named at the head of the column, the quotient would be 5.1.

Ry is a contraction for $dy/d\theta$, the rate of liberation of iodine; and Rx for $dx/d\theta$, the rate of formation of ferric salt, in the units defined above: $As = 5y$.

Influence of the acid on the rate Ry

By comparing Expts. 1, 3, 7; 2, 4, 8; 5, 11, 9; 12, 10; the influence of the concentration of the acid on the rate of liberation of iodine may be determined in the presence of three different quantities of potassium bichromate; in all cases the rate is very nearly proportional to the fourth power of the concentration of the acid. In this respect the reaction under consideration differs markedly from the reaction of chromic acid on either ferrous sulphate or potassium iodide alone; and, so far as I am aware, affords the first example on record where the rate is proportional to so high a power of the concentration of one of the reagents. Except in the polymerization of cyanic acid,¹ the highest power hitherto met with has been the second. As the rate is not changed by the addition of potassium sulphate, Expt. 28, the effect must be ascribed to the hydrogen ion.

Influence of the potassium bichromate on the rate Ry

Reducing the amount of chromate present from thirty to

¹ J. H. van 't Hoff. *Études de Dynamique Chimique*, page 94 (1884).

twenty equivalents, multiplies the time required for the liberation of a given quantity of iodine by 1.8 (Expts. 12, 5), while reduction from twenty to ten multiplies the time by 2.2 or 3 (Expts. 5, 1; 6, 2; 9, 7). If the rate is to be expressed as some power of the concentration of the bichromate, the first experiments would give

$$R_y = \text{const.} \times (\text{conc. bichromate})^{1.5}$$

and the others

$$R_y = \text{const.} \times (\text{conc. bichromate})^{1.3 \text{ to } 1.6}$$

Mr. DeLury has found that when potassium iodide is oxidized by chromic acid in the absence of ferrous sulphate, the rate is proportional to the first power of the concentration of the bichromate, while Expts. 34 and 35 of the present paper, and Tables III, VI, and VII of my article on the oxidation of ferrous sulphate show that in the absence of potassium iodide the rate of oxidation of ferrous sulphate varies between the first and the 1.8th power of the concentration of the bichromate.

Influence of the potassium iodide on the rate R_y .

Increasing the amount of potassium iodide present from 5 to 10 units (Expts. 14, 16; 15, 17) multiplies the rate by about 1.8, a second doubling of the concentration (10 to 20 units) (Expts. 16, 5; 17, 6) again multiplies the rate by about 1.7, while further increase from 20 to 30 units (Expts. 18, 5; 19, 6) multiplies the rate by 1.5. The effect produced by increasing the concentration of the potassium iodide is thus greatest when the concentration of the potassium iodide itself is greatest; rising to proportionality when KI = 20 to 30. The regular increase in the quotient $\theta \cdot T$ in the experiments compared, (Expts. 14, 15, 16) is too great to be ascribed to the change in the ratio between the concentrations of the iodide produced by the progress of the reaction. It is not due to difference in the rate of oxidation of the iron (Table XVII), it is too general to be accidental, and I have assured myself that it is not due to systematic errors in the analysis.

Influence of the ferrous salt on the rate R_y

Comparing the experiments in which the initial concentrations of the iron was 1.0 with those in which it was 0.5, it will be seen that the time corresponding to a given value of As in the former is half or little less than half that in the latter. A few experiments with other quantities of iron (Table X) give the same result.

When y is small, $\Delta y/\Delta \theta$ is approximately equal to $dy/d\theta$, the rate of liberation of iodine. In Table XI the smallest values of As have been collected from the previous tables; doubling F approximately doubles As .

The rate of liberation of iodine is therefore quite closely proportional to the concentration of the ferrous salt in the solution.

Influence of the products of oxidation on the rate R_y

To illustrate the great retarding effect of the products of oxidation on the rate of liberation of iodine, I have set side by side in Table XII the results of five experiments in which the initial concentration of the oxidation product (see page 8) was 0, 2.5, 3.3, 5.0, and 10.0, respectively.

The order of magnitude of the retardation is the same as in the oxidation of ferrous sulphate in the absence of iodides; and, as in the latter case, is due almost exclusively to the ferric salt — see Expts. 28, 29, 30, Table XIII.

In the absence of ferrous sulphate, ferric salts exert a decided accelerating action on the oxidation of potassium iodide by chromic acid. This is well shown by the experiments in Table XIV, for which I am indebted to Mr. R. E. DeLury. The ferric salt used was a fresh solution of iron alum; the amount taken is given in 10^{-5} gram-atoms of iron. The third and fourth experiments of the series prove that the difference between the first and the second is not altogether due to the ferrous salt produced by reduction of the iron alum; it must be ascribed in part to direct acceleration by the ferric salt.

If the product of oxidation, made up as described on page 8, be allowed to stand for a week, it gradually deposits a yel-

low-brown precipitate, and its retarding power is lessened; an illustration is given in Table XV, in which the time in days elapsed since the preparation of the oxidation product is given after "Age".

As in such dilute solutions the hydrolysis of the ferric sulphate must have been instantaneous,¹ this slow decrease in the power of retarding oxidation must be ascribed to changes in the colloidal hydrate, and might prove a means of throwing light on the latter.

Influence of certain other compounds of iron on the rate R_y

The influence exerted by ferric salts has been dealt with in the preceding section.

In Table XIII are given the results of experiments in which the power of Haemoglobin (from chickens' blood, 0.25 pct Fe), of Ferrosomatose (Bayer and Co., Elberfeld, 0.26 pct Fe), and of Potassium Ferrocyanide, to accelerate the oxidation of potassium iodide, was tested. In no case was any liberation of iodine observed. In the "Blanks" an amount of the standard ferrous solution equivalent to the total iron in the substance tested was added instead.

The great acceleration observed with ferrous sulphate is therefore due to the presence of the ferrous ion only.

In preliminary experiments on the oxidation of ferrous sulphate² I observed that sodium tartrate could not altogether stop the liberation of iodine in solutions containing ferrous salt; ferrous tartrate, therefore, acts as an accelerator, and if proper allowance were made for the effect of the tartrate on the H^+ -concentration, similar experiments might serve to determine the dissociation of this and other complex ferrous compounds.

The rate of oxidation of the ferrous salt, R_x

In the absence of any other feasible method of determining ferrous salts in the presence of ferric salt, chromic acid, etc., I have been forced to fall back on its power of accelerating the

¹ Zeit. phys. Chem. 21, 1 (1896).

² Jour. Phys. Chem. 7, 3 (1903).

oxidation of potassium iodide, and have already described a method of analysis based on that principle.¹

In order to obtain data for the calculation, a number of mixtures were made up with different initial quantities of iron, the concentrations of the other reagents being the same as in Expts. 5, 16, 14, 1, 9, and 23 respectively, and the amount of iodine liberated in 30 (or 60) minutes² was determined. The results are given in Table XVI.

In each of the Expts. 1, 2, 5, 6, 9, 14, 15, 16, 17, and 23, the numbers under As were subtracted from the value of As for 30 (or 60) minutes — in the case of Expt. 5, Table XVII, these differences are tabulated under "*Diff.*" — thus obtaining the amount of iodine liberated in from 22 to 30 (or 52 to 60) minutes in solutions containing initially $F-x$ units of ferrous sulphate; curves drawn from the data of Table XVI served to determine $F-x$. The values so obtained are given in Table XVII.

In this calculation there are two inaccuracies: — When $\theta = 8$, the difference $As (\theta = 8)$ minus $As (\theta = 30)$ gives the amount of iodine liberated in 22 minutes, while the curves were drawn for 30 minutes; $F-x$ for $\theta = 8$, however, is so small, and the reaction between $\theta = 8$ and $\theta = 30$ is so slow, that no serious error is introduced. Secondly, no account has been taken of the decrease in concentrations of the acid, bichromate, and iodide due to the progress of the reaction; this also is allowable, because as may be seen from Table XVIII, although the "total iodine" liberated during the oxidation of a given quantity of iron is not independent of the concentrations of the various reagents, yet the influence of small changes may safely be neglected. In the experiments for which $F-x$ was calculated the iodine liberated in 30 or 60 minutes respectively was practically identical with the "total iodine".

By means of the values of $F-x$ so obtained, the effect on Rx caused by changing the concentrations of the reagents may be ascertained.

¹ Jour. Phys. Chem. 7, 1 (1903).

² In Expt. 1, 90 minutes.

Doubling the concentration of the acid multiplies the rate of oxidation of the iron by 8 to 12 (between the 3d and 4th power of 2); Expts. 5 and 9, Table XVII.

Doubling the concentration of the bichromate doubles it (first power); Expts. 1 and 5, 2 and 6.

Increasing the concentration of the ferric salt greatly reduces the rate, the effect on R_x and on R_y being about the same; Expts. 23 and 5, Table XVII.

Increasing the concentration of the iodide first lowers the rate of oxidation of the iron ($KI = 0$ to $KI = 5.0$, Expts. 35, 14), then increases it again ($KI = 5.0$ to $KI = 20.0$, Expts. 14, 16, 5; 15, 17, 6).

With regard to the influence exerted by the concentration of the ferrous salt on the rate of its own oxidation, comparison of Expts. 5, 16, 14, 1 ($F = 1.0$) with Expts. 6, 17, 15, 2 ($F = 0.5$) shows that the time corresponding to a given value of x in the former is half that in the latter; *i. e.*, that doubling F doubles R_x (first power). In the absence of iodides, doubling F quadruples the rate (second power).

In order to make a direct comparison between R_x in the presence and in the absence of potassium iodide, the experiments of Table XIX were carried out with the same quantities of the other reagents as Expts. 1, 5, and 7, but without potassium iodide; $F-x$ was determined by means of Tables XIX, *b*, as already described.¹ From these experiments it appears, in accordance with the results of my former work, that in the absence of potassium iodide, doubling the acid ($KI = 0$) multiplies the rate by 4 (second power), and that doubling the bichromate ($KI = 0$) multiplies it by 2.8 (1.4th power).

Summary of the results of the measurements

The rate of liberation of iodine in the absence of ferrous salts (DeLury) is very nearly proportional to the concentration of the bichromate, and to the square of that of the acid. The relation between the rate and the concentration of the iodide can

¹ Jour. Phys. Chem. 7, 3 (1903).

be expressed by an equation of the form $Ry = mC + nC^2$. The oxidation is accelerated by ferric salts.

The rate of oxidation of ferrous sulphate in the absence of iodides is proportional to the second power of the concentration of the ferrous salt, and to the second power of that of the acid. The order of the reaction with respect to the bichromate is variable (1.4th to 1.8th). The oxidation is much retarded by ferric salts.

In presence of ferrous salts, the rate of liberation of iodine is proportional to the 1.3d to 1.6th power of the concentration of the bichromate, to the fourth power of that of the acid, to the first power of that of the ferrous salt, and to the first (or a less) power of that of the iodide. The oxidation is much retarded by ferric salts.

In presence of iodides, the rate of oxidation of ferrous sulphate is proportional to the first power of the concentration of the ferrous salt, to the third or fourth power of that of the acid, and to the first power of the concentration of the bichromate. Increase in the concentration of the iodide first decreases, then increases the rate.

The total iodine, y_x , liberated during the oxidation of a given quantity of ferrous sulphate (F) depends on the concentrations of the reagents and is only roughly proportional to the quantity of ferrous sulphate, y_x/F increasing as F decreases.

Having ascertained the facts with regard to the kinetics of the system : chromic acid, ferrous salt, iodide, it remains to compare them with certain theories which have been put forward to explain this and similar cases of catalysis. Of these the most prominent are, the Catalytic theory, the Active Oxygen theory, and the Peroxide theory, to which I have added a fourth, the Ferriodion theory.

The catalytic theory

In certain cases the rate of a reaction is changed by the presence of a foreign substance — platinum, for instance, to quote

a classical example — and since Berzelius' day it has been customary to ascribe the effect to "Catalysis" by the substance in question. In the oxidation of potassium iodide by chromic acid, however, it is obvious that much more than the rate is affected by the presence of ferrous sulphate; — the influence of the concentrations of the reagents on the rate is profoundly modified; so that the analogy with cases of simple catalysis is very slight.

The active oxygen theory

A number of instances of "induced oxidation" can be satisfactorily accounted for by the supposition that for every atom of oxygen taken up by the "inductor" — the ferrous salt in the present case — one, or some other whole number of atoms of oxygen become "active" and attack substances otherwise incapable of oxidation under the conditions of the experiment.

In the case under consideration the amount of iodine liberated during the oxidation of one atom of iron does not represent a whole number of atoms, and is not independent of the concentrations of the reagents; so that, in its simple form, the active oxygen theory is not applicable. When further developed, this theory passes into the

Peroxide theory,

according to which the primary product of the oxidation of the ferrous salt is a peroxide which afterwards reacts with the iodide and with the residual ferrous sulphate, forming ferric salts and liberating iodine.

This theory has found an able champion in Manchot, who is of the opinion¹ that "In every process of oxidation there is formed a *primary oxide*, which in general has the character of a peroxide." My own experiments which show that the rate of oxidation of ferrous sulphate is proportional to the square of the concentration of the ferrous salt, and to the first or a higher power of that of the bichromate, might fairly be quoted in support of this view; the molecular interpretation being that two molecules of ferrous sulphate enter into reaction "primarily" with one or

¹ Liebig's Ann. 325, 95 (1902).

more of the bichromate. The ratio 2 : 1 (2 : 1.8 fits the facts better) corresponds to the formula Fe_2O_5 , for which Manchot argues (see below).

In a paper entitled "Ueber Peroxydbildung beim Eisen" this author has published determinations of the "total iodine" liberated during the oxidation of certain quantities of ferrous sulphate by chromic acid in the presence of potassium iodide. Recalculated for a volume of 700 cc, and with the concentrations expressed in the units employed throughout this paper, these measurements are reproduced in Table XX. As will be noted, numbers iv, v, and vi were carried out under the same conditions; in viii and ix hydrochloric acid was used instead of sulphuric acid; the temperature in all cases was $0.2 - 0.6^\circ \text{C}$.

In his experiments, Manchot let 10-15 cc Fe^{10} ferrous sulphate flow into the mixture of the other reagents with the water; the addition of the iron took $1\frac{1}{2}$ to 2 minutes, during which the reacting mixture was well stirred. He draws the following conclusions: — "The experiments show that for one Fe two equivalents of iodine are set free, so that the ferrous salt consumes three equivalents of oxygen. This quantity is independent of the concentration of the chromic acid, of which in all the experiments (particularly No. ii and No. x) a residue remains.

"In the small variations in the amount of thiosulphate [As , Table XX] the secondary action of the peroxide on the ferrous salt is disclosed, as naturally it is not possible to add the ferrous salt in every case with exact uniformity. If this secondary reaction be favored, by pouring the chromic acid into the ferrous salt, so that the latter is in excess (particularly when more of it is used), much less iodine is liberated for one Fe oxidized, which furnishes the proof that the secondary reaction in question really takes place.

"The primary ferric peroxide is certainly not higher than Fe_2O_5 . For a considerable increase of the Acceptor [iodide] causes only an *inconsiderable* increase in the amount of thiosulphate [As]. The latter remains always a little below that

¹ Liebig's Ann. 325, 105 (1902).

corresponding to two equivalents of oxygen. This also speaks for the formula Fe_2O_4 ; because, other experiments with Acceptors show that it is not possible to prevent altogether this secondary reaction between ferrous oxide and peroxide."

In my own experiments (Table XVIII) y_x/F falls as low as 1.2 or 1.4 and changes with the concentrations much more than in those of Manchot. The same is true of y/x in the experiments of Table XVII. The explanation is to be found, not in "want of uniformity" in adding the ferrous sulphate — the mixing was complete and a homogeneous solution formed before the liberation of more than a trace of iodine — but in the data of Table XVIII itself, which show that increase in the concentrations of the reagents increases y_x/F . In Manchot's experiments the concentrations were much greater than in mine; his results approach more nearly to what is evidently the limiting ratio, viz: 2.

So far as I am aware, the peroxide theory has not yet been applied to explain in detail any particular case of catalysis where the rates have been measured, although it has become customary to assume the existence of "primary" peroxides in advancing qualitative explanations for incompletely studied reactions. In the succeeding paragraphs, therefore, I have developed the consequences of the theory for this particular case, and compared them with the results of the measurements.

The theory assumes the occurrence of three different reactions in the solution: formation of the peroxide, action of the peroxide on the iodide, and action of the peroxide on the residual ferrous salts. Of these, the first may be regarded as the reaction whose rate is measured, and the others as following quickly after it, otherwise the peroxide would accumulate in the solution; moreover, the slow disappearance of the ferrous salt has been established by direct experiments with potassium ferrocyanide.

Representing by p the quantity of the peroxide which contains one atom of iron ($\frac{1}{2}\text{Fe}_2\text{O}_5$ if Manchot's formula be adopted), and by n the number of molecules of potassium iodide or ferrous sulphate with which that quantity of peroxide reacts ($n = 2$,

according to Manchot) the last two reactions may be represented by the following chemical equations:—



and



Writing dp for $\partial p / \partial \theta \cdot d\theta$, the amount of peroxide formed in a unit of time, d_1p for the amount entering into reaction i , and d_2p for the amount entering into reaction ii , also in a unit of time, the assumption that the peroxide is destroyed as soon as it is formed may be expressed by the equation

$$dp = d_1p + d_2p.$$

The amount of iodine liberated, dy , if expressed in equivalents, is obviously equal to nd_1p , while the ferric salt formed,

$$dx = d_1x + d_2x = d_1p + (n+1)d_2p$$

The rates of the two reactions i and ii above, must, in general, depend on the concentrations of the iodide and ferrous salt; adopting the form most in harmony with the prevalent practice in chemical kinetics, the ratio of the two rates may be set proportional to the quotient of some powers of the concentrations.¹

$$d_1p / d_2p = k(F-x)^r (C-y)^r \dots\dots\dots (1)$$

and the rate of formation of peroxide to the r -th power of the concentration of the ferrous salt

$$dp / d\theta = K(F-x)^r \dots\dots\dots (2)$$

From these equations the following expressions for the rate of liberation of iodine,

$$Ry = \frac{dy}{d\theta} = \frac{dy}{dp} \cdot \frac{dp}{d\theta} = \frac{nd_1p}{d_1p + d_2p} \cdot \frac{dp}{d\theta} \left\{ \dots\dots\dots (3) \right.$$

$$\left. \frac{Kn(C-y)^r(F-x)^r}{(C-y)^r + k(F-x)^r} \right\}$$

and for the "total iodine"

¹ C represents the initial concentration of the iodide, and F that of the ferrous salt. K in Equation 2 is a function of the concentrations of the acid and bichromate

$$y_r = \int_0^{C-y} dy \int_0^t \frac{n(C-y)}{k(n+1)(F+1)} dv \dots\dots\dots (4)$$

may be obtained.

I have integrated the latter expression for three particular cases, viz: (i) $t = s = 1$; (ii) $s = 2, t = 1$; (iii) $s = t = 2$; introduced experimentally determined values for y_r , solved for n and k , and then by means of Equation (3) computed the relative rates for different concentrations of potassium iodide. The results are tabulated for comparison with the experiments. Finally, I have shown that no other assumptions as to the values of s and t would bring the results of the calculations into better agreement with the experimental numbers.

Case i. $s = t = 1$. — Substituting, and integrating (treating $C-y$ as constant, and equal to C) the expression for the "total iodine" becomes

$$y_r = \frac{nC}{k(n+1)} \cdot \log n \frac{C+kF(n+1)}{C} \dots\dots\dots (5)$$

Making use of the results of Expt. 5: $F = 1.0, C = 20, y_r = 1.56$, and Expt. 14: $F = 1.0, C = 5, y_r = 1.20$, numerical values for n and k may be obtained. As, in Expt. 14, $C-y$ falls from 5.0 to 3.9, while the integral was obtained under the assumption that $C-y = C$, I have obtained limits for n and k by setting $C = 5$ in one calculation, and $C = 4$ in a second.

The values are,

$$n = 1.77 \text{ and } 1.71 \quad k = 1.91 \text{ and } 1.44 \dots\dots\dots (6)$$

and by introducing them into Equation (3), and at the same time setting $s = t = 1, r = 0$, and $F = 1$, the (initial) rates of liberation of iodine in the presence of different concentration of the iodide were calculated.

The results, multiplied by an arbitrary constant, are given in Table XXI, Ry for $C = 5$ has been set 100 to facilitate comparison.

Increase in the concentration of the iodide from 5 to 30 adds

but 30 percent to the rate; the experiments show that 300 percent is added.

Calculating backwards, setting $Ry(C = 20) = 2.4$, $Ry(C = 5)$ —see Expts. 5 and 14—there follows, $k = 17.5$; whence, assuming $n = 2$ (Manhot)

$$y_c (C = 5) = 0.46; \text{ obs. } 1.20$$

$$y_c (C = 20) = 0.87; \text{ obs. } 1.56$$

Case ii. $s = 2, t = 1$.—Substituting in Equations (3) and (4), setting $C = y = C$, and carrying out the integration in Equation (4) there results:

$$Ry = dy d\theta \frac{KnC(F-x)^n}{C^n(F-x)^n} \dots\dots\dots (7)$$

and

$$y_c = \frac{1}{1 + k(n+1)} \cdot \tan^{-1} \frac{K(x+1) \cdot F}{1 + C} \dots\dots\dots (8)$$

Introducing the same pair of values as in Case i, and solving for n and k ,

$$n = 1.82 \quad k = 3.78 \dots\dots\dots (9)$$

(Only the upper limit for k —the more favorable—being computed.) Initial values of Ry , ($x = 0$), (Table XXII) have been calculated from (7) and (9), setting $Ry(C = 5) = 100$, as before. The results are much the same as in Case i; widely different from the experiment.

Case iii. $s = t = 2$.

$$Ry = \frac{KnC^2(F-x)^n}{C^n(F-x)^n} \dots\dots\dots (10)$$

and

$$y_c = \frac{Cn}{1 + k(n+1)} \cdot \tan^{-1} \frac{k(n+1) \cdot F}{C} \dots\dots\dots (11)$$

whence $n = 1.80$, $k = 72.3$, and the number under "initial Ry ($F = 1.0$)" in Table XXIII.

The results of the calculation are in better agreement with the experiments than those of *i* and *ii*; although in the Table

the first increment of C has more effect than the last, while in reality the reverse is the case. The agreement, such as it is, however, is due to the circumstance that F has been set equal to unity, and x to zero in making the computation. If F be set 0.5, and $x = 0$, no value of r can be found that will make Ry half what it is when $F = 1.0$; this is evident on inspecting Equation (10); to show how wide the discrepancy may be in particular cases, Ry has been calculated for $r = 1$ and $r = 2$, and the results entered in Table XXIII.

Similar want of success must necessarily attend the substitution of other values for s and t ; Equation (3) can be brought into partial accordance with the experiments only if $t = 1$, and k is large enough to annihilate the term $(C-y)^2/k$ in the denominator¹. This would make y_x proportional to C , and less than F , neither of which is supported by the observations.

The calculations of the preceding paragraphs show that the Peroxide Theory cannot reconcile the results of the experiments on the rate of liberation of iodine with those on the "total iodine". This however is not the only respect in which it fails. Three others may be mentioned briefly.

First, the influence of the iodide on the rate of oxidation of the ferrous salt. If the liberation of iodine be the result of a secondary reaction between peroxide and iodide, increase in the concentration of the iodide can cause increase in the rate of liberation of iodine only by causing a corresponding increase in the "total iodine" and decrease in the rate at which ferric salt is formed. The measurements show that doubling the concentration of the iodide almost doubles Ry , and slightly *increases* Rx .

Second, the influence of the iodide on the rate of liberation of iodine. According to the theory, each successive increment of the iodide should have less effect than the preceding, until finally, when $y_x = 2F$, further addition of iodide should leave the rate unchanged. According to the experiments, the influence of the iodide increases with its concentration.

Finally, it has been established in the experimental part of this paper, that in the absence of iodides, doubling the concentrations of either the acid or the ferrous salt quadruples the rate

¹ After dividing both numerator and denominator by k .

at which the iron is oxidized; while in their presence doubling the concentration of the acid multiples it by eight or twelve, and doubling that of the iron, by two. It is hard to see how these facts can be accounted for by a theory which assumes that the "primary reaction" is the same in both cases.

In short, the "Peroxide Theory" was set up before the rate measurements were made, and in attempting to explain them it breaks down.

The ferroiodion theory

If it be assumed that the iodide takes part in the reaction whose rate is measured, many of the difficulties met with in the previous paragraphs may be avoided. The chromic acid may be represented, for instance, as acting on ferrous iodide, forming ferric salt and iodine:



In view of the results of the rate measurements, the "primary reaction" may be considered to take place between the ions



and the fact that, in general, less than two atoms of iodine are liberated for each atom of iron oxidized may be accounted for by assuming simultaneous direct action of the chromic acid on the ferroion.

This theory offers an explanation for all the principal results of the experimental investigation.

By introducing a new reaction (Equation *i*) in solutions containing both ferrous salts and iodides, it accounts for the fundamental differences between the oxidation of ferrous sulphate or potassium iodide alone, and in solutions containing both.

By including potassium iodide in the primary reaction, it is able to account for proportionality between *Ry* and the concentration of that reagent, while avoiding the difficulties raised by the Peroxide Theory. The decrease in *Rx* consequent on the first addition of potassium iodide can be ascribed to diminution

in the number of Fe ions (formation of FeI, Ferriodion), while the subsequent increase is due to increase in the rate of reaction (i) brought about by increase in the concentration of the iodide.

Finally, by admitting direct action between chromic acid and ferrous sulphate, the Ferriodion Theory explains the variations in the "total iodine" liberated during the oxidation of a given quantity of iron. Increasing the concentration of the acid or of the iodide increases the rate of the main reaction over that of the other, and thus causes y_r to approach more nearly its limiting value, $2F$; while the diminution in y_r/F as F increases is caused by the rate of oxidation of ferrous sulphate being proportional to the square of its concentration, while the rate of formation of ferric salt by reaction (i) is proportional to the first power only.

This theory, however, like the Peroxide Theory, affords no explanation of the variable "order" of the reaction with respect to the bichromate, and it exaggerates somewhat the influence of the iodide. Doubling the concentration of the potassium iodide ought to double the rate of liberation of iodine; Expts. 5, 14, and 16 show that this condition is complied with only when $C = 20$ or larger; between $C = 5$ and $C = 20$, doubling C multiplies the rate by 1.7 or 1.8 only.

A simple calculation reveals a similar discrepancy in dy/dx . The reactions assumed are,



and



If A , B , C , and F be the quantities of acid, bichromate, iodide, and ferrous salts (in equivalents) initially present, x and y the ferric salt and free iodine already formed, d_1x , and d_2x the ferric salt formed in unit time by reactions i and ii respectively, and a the fraction of the residual ferrous salt uncombined with iodine; the rates of the two reactions at the beginning of an experiment, before x and y are large enough to be taken into consideration ("initial rates") may be written

$$R_1 = d_1 x' d\theta = \frac{1}{2} dy d\theta = k_1 A^2 BCF(1-a) \dots\dots (12)$$

$$R_2 = d_2 x' d\theta = k_2 A^2 BF^2 a^2 \dots\dots\dots (13)$$

and the initial ratio,¹

$$\frac{ay}{ax} = \frac{2k_1 A^2 C(1-a)}{k_2 A^2 C(1-a) + a^2 F} \dots\dots\dots (14)$$

in which $k = k_1/k_2$.

As y/x changes but slowly in the experiments for which x has been calculated, it is possible to obtain the initial value of dy/dx from the Tables with a fair degree of approximation. In Expt. 5 ($A, 10$; $B, 20$; $C, 20$; $F, 1.0$) it is 1.3. Introducing this value in Equation (14), there follows

$$a^2 k(1-a) = 1.077; \text{ and } dy/dx = 0.63 \text{ for } C = 10, \\ \text{obs. } 0.9 \text{ (Expt. 16),}$$

the observed change being less than that called for by the theory.²

To bring the Ferriodion Theory into still better accord with the experimental results, it must evidently be modified in some manner which, while leaving the main feature of the theory intact, will lessen the influence of the iodide a little, especially when the concentration of that reagent is low. As the principal reaction (oxidation of FeI) can hardly be interfered with without sacrificing the main points of agreement with the experiments, the remedy must be sought in introducing a third or fourth simultaneous reaction, or in modifying the subsidiary reaction already admitted, viz., the direct oxidation of ferrous salt.

¹ By introducing x and y , and integrating between the limits $x = 0$ and $x = F$, an expression for y_r may be obtained; it is not however of a convenient form for computations.

² In computing dy/dx by Equation 14 it must be noted that $a^2(1-a)$ is a function of C ; they are connected by the equation of equilibrium

$$Ca = \text{Const} \cdot (1-a),$$

corresponding to the reaction



If a is large, $(1-a)a^2$ is proportional to C ; this assumption — the most favorable one — has been made computing dy/dx for $C = 10$ above.

If it be supposed that the "primary" product is a peroxide — the evidence of the rate measurements (oxidation of FeSO_4 , page 16) in favor of this hypothesis remains, although, as has been shown, that drawn from the liberation of iodine will not bear examination — increase in the concentration of the iodide, while increasing the rate of the main reaction, will lessen the rate of the "direct" oxidation, by converting Fe^{++} ions into FeI^+ , and may thus diminish the supply of iodine arising from secondary decomposition of the peroxide. The rate of liberation of iodine will thus be less than proportional to the concentration of the iodide, until the latter is great enough to dispose of all of the Fe^{++} ions. From then on, R_y will be proportional to C .

In conclusion, I wish to express my thanks to Prof. W. Lash Miller for the interest he has displayed in this research.

*The University of Toronto,
April, 1903.*

TABLES

TABLE I.

Ac, 10; Cr, 10; KI, 20; Ox, 5; V, 700

Expt. 1. F 1.0

Expt. 2. F 0.5

θ	As	Cr 20	θT	Ac 15	θT	θ	As	Cr 20	θT	Ac 15	θT
1	0.80	0.35	2.9	0.25	4.0	2	0.75	0.80	2.5	0.5	4.0
2	1.40	0.7	2.9	0.5	4.0	4	1.40	1.55	2.6	1.0	4.0
4	2.40	1.35	2.9	0.90	4.4	8	2.15	2.90	2.8	1.7	4.7
8	3.50	2.6	3.0	1.60	5.0	20	3.60	—	—	—	—
16	4.95	—	—	—	—	30	3.80	—	—	—	—
25	5.55	—	—	—	—	90	4.00	—	—	—	—
30	5.65	—	—	—	—	—	—	—	—	—	—
60	6.85	—	—	—	—	—	—	—	—	—	—
90	7.15	—	—	—	—	—	—	—	—	—	—
120	7.10	—	—	—	—	—	—	—	—	—	—

Calc: 1st, 2.0; 4th, 5.1

1st, 2.0; 4th, 5.1

Blanks: 22°; 28*; 42, As 0.2; 60, As 0.35; 90, As

0.50; 120, As - 0.75

TABLE II.

Ac, 15; Cr, 10; KI, 20; Ox, 5; V, 700

Expt. 3. F 1.0

Expt. 4. F 0.5

θ	As	Cr 20	θT	Ac 20	θT	θ	As	Ac 20	θT
0.5	1.55	0.25	2.0	0.18	2.9	0.5	0.80	0.17	3.0
1	2.55	0.40	2.5	0.30	3.3	1	1.45	0.35	3.0
2	4.15	0.80	2.5	0.70	2.9	2	2.45	0.7	3.0
4	5.55	1.60	2.5	1.30	3.1	4	3.45	1.5	2.7
8	6.90	3.10	2.6	2.20	3.6	25	4.35	—	—
25	8.35	—	—	—	—	—	—	—	—

Calc: 1st, 2.0; 4th, 3.2

4th, 3.2

Blanks: 25°; 29*; 38**

TABLE III.

Ac, 10; Cr, 20; KI, 20; Ox, 5; V, 700

Expt. 5. F 1.0								Expt. 6. F 0.5					
θ	As	Cr 30	θ T	Ac 15	θ T	KI 30	θ T	As	Cr 20	θ T	KI 30	θ T	
0.5	1.05	0.25	2.0	0.1	5	0.3	1.7	0.40 ¹	0.2	2.5	0.3	1.7	
1	1.90	0.55	1.8	0.2	5	0.7	1.4	1.00	0.50	2.0	0.8	1.3	
2	3.10	1.05	1.9	0.5	4	1.4	1.4	1.75	1.20	1.7	1.7	1.2	
4	4.30	2.10	1.9	0.9	4.4	2.7	1.5	2.50	2.0	2.0	3.0	1.3	
8	5.60	4.40	1.8	1.6	5	5.5	1.5	3.30	4.0	2.0	5.0	1.6	
20	7.10	—	—	—	—	—	—	4.05	—	—	—	—	
30	7.70	—	—	—	—	—	—	4.20	—	—	—	—	
120	7.85	—	—	—	—	—	—	—	—	—	—	—	
Calc: 1st, 1.5; 4th, 5.1								1st, 1.5		1st, 1.5		1st, 1.5	
Blanks: 20°; 28*; 120, As = 0.65													

TABLE IV.

Ac, 20; Cr, 10; KI, 20; Ox, 5; V, 700

Expt. 7. F 1.0				Expt. 8 F 0.5	
θ	As	Cr 20	θ T	θ	As
0.25	2.15	0.1	2.5	0.25	1.15
0.5	3.50	0.2	2.5	0.5	2.10
1	4.75	0.35	3.0	1	2.95
2	6.70	0.82	2.5	2	3.90
4	7.80	1.6	2.5	4	4.05
8	8.55	3.6	2.2	25	4.90
30	8.80	—	—	—	—

Calc: 1st, 2.0

Blanks: 20°; 32°

¹ Probably too low; does not fall on curve.

TABLE V.

KI, 20; Ox, 5; F, 1.0; V, 700

Expt. 9 Ac, 20; Cr, 20		Expt. 10 Ac, 15; Cr, 30		Expt. 11. Ac, 15; Cr, 20					
θ	As	θ	As	θ	As	Ac 20	θ T	Cr 30	θ T
0.25	4.05	0.5	4.45	0.5	3.00	0.15	3.3	0.22	2.2
0.5	5.75	1	5.90	1	4.00	0.30	3.3	0.55	1.9
1	7.15	2	7.15	2	6.00	0.60	3.3	1.05	1.9
2	8.00	4	8.00	4	7.50	1.30	3.1	2.50	1.6
8	8.60	20	8.35	30	8.35	—	—	—	—
20	8.80	—	—	—	—	—	—	—	—
30	8.75	—	—	—	—	—	—	—	—
120	8.50	—	—	—	—	—	—	—	—

Calc:

4th, 3.1 1st, 1.5

Blanks (Expt. 9): 27°; 32*; 75, As = 0.50; 120, As = 0.70

Blanks (Expt. 10): 27°; 38*; 48**

Blanks (Expt. 11): 26°; 40*

TABLE VI.

Ac, 10; Cr, 30; KI, 20; Ox, 5; V, 700

Expt. 12. F = 1.0				Expt. 13 F = 0.5	
θ	As	Ac 15	θ T	θ	As
0.5	1.75	0.08	6.2	0.5	0.90
1	2.95	0.15	6.6	1	1.55
2	4.15	0.4	5	2	2.45
4	5.30	0.8	5	4	3.30
25	7.75	—	—	30	4.55
30	7.55	—	—	—	—

Calc:

4th, 5.1

Blanks: 27°; 38*; 48**

TABLE VII.

Ac, 10; Cr, 20; KI, 5; Ox, 5; V, 700

Expt. 14. $\bar{P}$ 1.0Expt. 15. $\bar{V}$ 0.5

θ	As	KI 10	θT	θ	As	KI 10	θT
1	0.95	0.6	1.7	2	0.90	1.30	1.5
2	1.55	.1	1.8	4	1.35	2.1	1.9
4	2.40	2.3	1.8	8	2.05	3.9	1.8
8	3.40	4.2	1.9	60	3.60	—	—
60	5.65	—	—	—	—	—	—
120	5.75	—	—	—	—	—	—
180	6.00	—	—	—	—	—	—
Calc :	1st, 2.0			1st, 2.0			
Blanks :	60°; 180*						

TABLE VIII.

Ac, 10; Cr, 20; KI, 10; Ox, 5; V, 700

Expt. 16. F 1.0

Expt. 17. F 0.5

θ	As	KI 20	θT	θ	As	KI 20	θT
1	1.40	0.7	1.4	1	0.55	0.7	1.4
2	2.20	1.2	1.7	2	1.30	1.4	1.4
4	3.30	2.3	1.8	4	2.05	2.7	1.5
8	4.30	4.0	2.0	8	2.95	5.5	1.4
60	6.80	—	—	60	4.20	—	—
120	7.00	—	—	—	—	—	—

Calc: 1st, 2.0
Blanks: 60°; 120, As = 0.10

TABLE IX.

Ac, 10; Cr, 20; KI, 30;
Ox, 5; V, 700

Expt. 18		Expt. 19	
F 1.0		F 0.5	
θ	As	θ	As
0.5	1.50	0.5	0.60
1	2.40	1	1.10
2	3.70	2	1.85
4	5.10	4	2.95
20	7.75	20	4.55
105	7.80	—	—

Blanks: 16°; 21*; 105, As 1.40

TABLE X.

Expt. 20. Ac, 10; Cr, 20; KI, 20; Ox, 5; F, 2.0; V, 700

θ	As	F 1.5	θ T	F 1.0	θ T	F 0.5	θ T
0.25	1.40	0.36	0.7	0.7	0.36	1.5	0.17
Calc:		1st, 0.75		1st, 0.5		1st, 0.25	

Expt. 21. Ac, 10; Cr, 20; KI, 20; Ox, 5; F, 1.5; V, 700

θ	As	F 1.0	θ T	F 0.5	θ T
0.25	0.95	0.45	0.55	1.0	0.25
0.5	1.90	1.0	0.50	2.3	0.13
Calc:		1st, 0.67		1st, 0.33	

Expt. 22. Ac, 20; Cr, 10; KI, 20; Ox, 5; F, 0.25; V, 700

θ	As	F 0.5	θ T	F 1.0	θ T
0.5	1.0	2	2.5	0.1	5
Calc:		1st, 2.0		1st, 4.0	

TABLE XI.

θ	As (F = 1.0)	As (F = 0.5)	Expt. (F = 1.0)	Expt. (F = 0.5)
2.0	1.40	0.75	1	2
0.5	1.55	0.80	3	4
0.5	1.05	0.40 ¹	5	6
0.25	2.15	1.15	7	8
0.5	1.75	0.90	12	13
2.0	1.55	0.90	14	15
1.0	1.40	0.65	16	17
0.5	1.50	0.60	18	19

TABLE XII.

Ac, 10; Cr, 20; KI, 20; F, 1.0; V, 700

Expt. 23 Ox, 0		Expt. 24 Ox, 2.5		Expt. 25 Ox, 3.3		Expt. 26 Ox, 5.0		Expt. 27 Ox, 10.0	
θ	As	θ	As	θ	As	θ	As	θ	As
0.5	3.95	0.5	1.50	1	2.25	0.5	1.05	1	1.40
1	5.00	1	2.40	2	3.40	1	1.90	2	2.25
2	5.85	2	4.80	4	4.80	2	3.10	4	3.55
4	6.30	—	—	—	—	4	4.30	8	4.85
20	7.20	—	—	—	—	8	5.60	16	6.50
43	7.40	—	—	—	—	20	7.10	—	—
—	—	—	—	—	—	30	7.75	—	—
—	—	—	—	—	—	120	7.85	—	—

¹ See footnote Table III.

In Table XI. "As (F = 1.0)" signifies the reading at time θ when F = 1.0; "Expt. (F = 1.0)" is the number of the experiment from which the data were taken. Similarly with "As (F = 0.5)" and "Expt. (F = 0.5)."

TABLE XIII.

KI, 20; V. 700

Expt.	Addition	Ac	Cr	Ox	F	θ	As	Blank
28	20 cc F 40 K_2SO_4	10	20	0	1.0	1	4.90	5.00
29	5 cc F 20 $Cr_2(SO_4)_3$ ¹	10	20	0	1.0	1	4.90	5.00
30	10 cc <i>n</i> . 100 Iodine	10	20	5	1.0	8	5.55	5.60
31	0.1 g Haemoglobin	20	10	5	0	5	0.00	0.80
32	1.0 g Ferrosomatoase	10	20	0	0	15	0.00	7.00
33	0.2 g $K_4Fe(CN)_6$	10	20	0	0	20	0.00	7.20

TABLE XIV.

KI, etc. in gram-mols $\times 10^{-5}$; Temp. 30° C; V. 100 cc

Expt.	KI	H ₂ SO ₄	K ₂ Cr ₂ O ₇	Fe'''	Fe''	θ	Thio.
<i>i</i>	142	240	1.968	0	0	5	0.90
<i>ii</i>	142	240	1.968	25	0	5	13.60
<i>iii</i>	142	240	0	25	0	5	4.07
<i>iv</i>	142	240	1.968	0	4.07	5	8.61

TABLE XV.

Ac, 10; Cr, 20; KI, 20; F, 1.0; V, 700; θ 4

Age	5	11	21	22	140
As	3.73	4.63	4.73	4.72	5.70

TABLE XVI.

F	Expt. 5B θ 30	Expt. 16B θ 60	Expt. 14B θ 60	Expt. 11B θ 90	Expt. 9B θ 30	Expt. 23B θ 30
0	0.00	0.00	0.00	0.00	0.00	0.00
0.2	1.85	1.85	1.70	1.80	2.05	1.75
0.4	3.50	3.50	3.00	3.25	3.80	3.15
0.6	5.00	4.85	3.90	4.45	5.50	4.40
0.8	6.85	5.85	4.50	6.20	7.00	—
1.0	7.70	6.80	5.65	7.10	8.75	7.30

¹ Chrome alum was used.

Results rather uncertain, because of large reading in "blank"

TABLE XVII.

Expts. 5 and 6. Ac, 10; Cr, 20; KI, 20; Ox, 5; V, 700;

Expt. 5, F 1.0; Expt. 6, F 0.5.

Expts. 16 and 17. Ac, 10; Cr, 20; KI, 10; Ox, 5; V, 700;

Expt. 16, F 1.0; Expt. 17, F 0.5.

Expts. 14 and 15. Ac, 10; Cr, 20; KI, 5; Ox, 5; V, 700;

Expt. 14, F 1.0; Expt. 15, F 0.5.

Expt. 35. Ac, 10; Cr, 20; KI, none; Ox, 5; F 1.0; V, 700.

Expts. 1 and 2. Ac, 10; Cr, 10; KI, 20; Ox, 5; V, 700;

Expt. 1, F 1.0; Expt. 2, F 0.5.

Expt. 9. Ac, 20; Cr, 20; KI, 20; Ox, 5; F 1.0; V, 700.

Expt. 23. Ac, 10; Cr, 20; KI, 20; Ox, none; F 1.0; V, 700.

θ	Expt. 5		Expt. 16		Expt. 14		Expt. 35		Expt. 1		Expt. 9		Expt. 23	
	As	Diff.	F	x	F	x	F	x	F	x	F	x	F	x
0.25	—	—	—	—	—	—	—	—	—	—	0.50	—	—	—
0.5	1.05	6.65	0.85	—	—	—	0.82	—	—	—	0.30	0.44	—	—
1	1.90	5.80	0.72	0.62	0.80	0.70	0.84	0.14	0.33	—	0.14	0.33	—	—
2	3.10	4.60	0.54	0.55	0.66	0.54	0.75	0.07	0.18	—	0.07	0.18	—	—
4	4.30	3.40	0.38	0.40	0.47	0.34	0.60	—	0.12	—	0.02	—	—	—
8	5.60	2.15	0.24	0.26	0.37	—	0.44	—	—	—	—	—	—	—
30	7.70	—	—	—	—	—	—	—	—	—	—	—	—	—

θ	Expt. 6		Expt. 17		Expt. 15		Expt. 2	
	F	x	F	x	F	x	F	x
0.5	0.44	—	—	—	—	—	—	—
1	0.36	0.39	—	—	—	—	—	—
2	0.27	0.30	—	—	0.34	0.40	—	—
4	0.18	0.21	—	—	0.26	0.32	—	—
8	0.08	0.12	—	—	0.18	0.20	—	—

TABLE XVIII.

Ox. 5; F, 1.0; Vol. 700 cc

Expt.	Ac	Cr	KI	θ	As
1	10	10	20	120	7.10
3	15	10	20	25	8.35
7	20	10	20	30	8.80
5	10	20	20	120	7.85
11	15	20	20	30	8.35
9	20	20	20	30	8.75
12	10	30	20	25	7.75
10	15	30	20	20	8.35
14	10	20	5	180	6.00
16	10	20	10	120	7.00
5	10	20	20	120	7.85
18	10	20	30	105	7.80

TABLE XIX.

KI, none; Ox. 5; F, 1.0; V, 700

θ	Expt. 34 Ac, 10; Cr, 10			Expt. 35 Ac, 10; Cr, 20			Expt. 36 Ac, 20; Cr, 10		
	As	$1-x$	k_1^1	As	$1-x$	k_2	As	$1-x$	k_2
0.0	4.45	1.0	—	4.45	1.0	—	6.70	1.0	—
0.5	3.65	0.90	0.22	3.65	0.82	0.44	5.18	0.78	0.56
1.0	3.10	0.85	0.17	3.10	0.70	0.43	4.08	0.61	0.64
2.0	2.75	0.75	0.16	2.40	0.54	0.43	3.07	0.45	0.61
4.0	2.25	0.62	0.16	1.50	0.34	0.48	2.15	0.32	0.62

TABLE XIX.*b*

FeSO ₄	1.0	0.8	0.7	0.6	0.4	0.3	0.25	0.0
As (Expt. 34)	4.45	—	2.62	—	1.57	—	—	0.0
As (Expt. 35)	4.42	3.55	—	2.85	1.90	—	1.20	0.0
As (Expt. 36)	6.70	—	4.70	—	2.90	2.17	—	0.0

$$^1k_2 = \frac{1}{\theta} \cdot \frac{x}{1-x}$$

TABLE XX.

No.	Ac	Cr	KI	F	As	As calc. (2equiv.)
<i>i</i>	230	16	26	5.16	47.2	51.8
<i>ii</i>	230	21	26	5.15	47.3	51.7
<i>iii</i>	440	16	47	5.02	47.8	50.4
<i>iv</i>	225	16	48	5.11	47.3	51.3
<i>v</i>	225	16	48	5.11	48.2	51.3
<i>vi</i>	225	16	48	5.11	47.9	51.3
<i>vii</i>	225	16	48	5.11	47.8	51.3
<i>viii</i>	225	16	48	5.11	48.7	51.3
<i>ix</i>	440	16	47	5.14	48.6	51.6
<i>x</i>	230	20	48	5.15	50.0	51.7

TABLE XXI.

C	Initial <i>Ry</i> (calc.)		Initial <i>Ry</i>
	<i>k</i> = 1.91	<i>k</i> = 1.44	Obs.
5	100	100	100
10	116	113	170
20	126	119	280
30	131	127	405

TABLE XXII.

C	Initial <i>Ry</i>	
	Calc.	Obs.
5	100	100
10	129	170
20	152	280
30	162	405

TABLE XXIII.

C	Initial Ry (calc.)				
	F = 1.0	F = 0.5 $r = 1$		F = 0.5 $r = 2$	
		Ry	Ratio	Ry	Ratio
5	100	112.8	1.13	56.4	0.56
10	227	164.8	0.73	82.4	0.36
20	331	186.2	0.56	93.1	0.28
30	363	190.8	0.53	95.4	0.26
Obs.	—	—	0.5	—	0.5

